John von Neumann Institute for Computing

Laserinduced Desorption of CO from Chromiumoxide

S. Thiel, M. Pykavy, T. Klüner, V. Staemmler, H.-J. Freund

published in

Modern Methods and Algorithms of Quantum Chemistry,
J. Grotendorst (Ed.), John von Neumann Institute for Computing, Jülich, NIC Series, Vol. 2, ISBN 3-00-005746-3, p. 17, 2000.

http://www.fz-juelich.de/nic-series/

Laserinduced Desorption of CO from Chromiumoxide

S. Thiel, M. Pykavy, T. Klüner, V. Staemmler[†], H.-J. Freund

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Abt. Chemische Physik, Faradayweg 4-6, 14195 Berlin

[†] *Ruhr-Universitaet Bochum, Lehrstuhl fuer Theoretische Chemie, Universitaetsstrasse 150, 44801 Bochum*

In recent experiments the rotational alignment of the laserinduced non-thermal desorption of CO adsorbed on a an epitaxially grown film of Cr_2O_3 (0001) has been studied[1]. At low rotational quantum numbers J the molecules desorb like a helicopter (J-vector perpendicular to the surface) while at high J-values a cartwheel motion is preferred (J-vector parallel to the surface).

These stereodynamical effects and the experimental state resolved velocity distributions of the desorbing species are simulated using a time dependent wave packet method in four dimensions. As a prerequisite for these investigations substantial effort had been neccessary in the field of development and implementation of efficient algorithms for the solution of the time-dependent Schroedinger equation in many dimensions. Up to four dimensional wave packet calculations including diabatic coupling elements and arbitrary laser pulses can be performed using the computer equipment available in our department. A high dimensional version of our code for the use on massively parallel platforms (Cray T3E) has been developed.

As a basis for this quantum mechanical treatment of nuclear motion of the adsorbed molecule a fourdimensional ab initio potential energy surface for the electronic ground state of this adsorbate-substrate system has been calculated in an embedded cluster approach[2]. Different slices through electronically excited states are calculated in a configuration interaction scheme and the influence of several coordinates on the final state distributions is examined[3]. To improve the quality of these quantumdynamical simulations, a fourdimensional ab initio potential energy surface for an electronically excited state is modelled at the moment. The basis for this PES is an internal $5\sigma - 2\pi$ excitation within the adsorbed CO molecule.

References

[1] I. Beauport, K. Al-Shamery, H.-J. Freund. *Chem. Phys. Lett.*, 256, 641, 1998

[2] M. Pykavyi. PhD-Thesis, Ruhr Universitaet Bochum, 1999

[3] S. Thiel, T. Klüner, H.-J. Freund. to be published